



Direct combination of hydrogen evolution from water and methane conversion in a photocatalytic system over Pt/TiO₂



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ABSTRACT

The CH₄ conversion under ambient condition remains a challenge over the past years, and the production of the ideal clean energy of H₂ is considered as an alternative method to meet the requirement of sustainable development. Herein, a new photocatalytic reaction system involved H₂ evolution from aqueous water and CH₄ conversion is established over Pt/TiO₂. The synergistic effect between the two reactions of H₂ production and CH₄ conversion brings up the considerable quantum efficiencies of H₂ production to 4.7% without sacrificial agent and CH₄ conversion (the main products are C₂H₆ and CO₂) to 3.3% simultaneously. The introduction of Pt on the surface of TiO₂ particles facilitates the activation of CH₄ and •OH that can assist to produce methyl radical (•CH₃), afterwards more C₂H₆ (61.7% selectivity) is formed.

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1. Introduction

Methane (CH₄), occupying the primary component of natural gas, is nearly ubiquitous in the world. As a fuel, the commercial use of CH₄ by directly burning will result in much worse global warming than CO₂ [1,2]. Recent, the conversion of CH₄ to other high value-added products has received increasing attention because of their sustainability for energy and environment [3–14]. These processes often demand the high pressure or high temperature reaction conditions. Photocatalysis technology is recognized as an alternative solution to meet the green conversion of CH₄, since the solar energy is by far the largest exploitable resource [15]. Some important achievements, such as non-oxidative coupling of CH₄ to higher hydrocarbons (ethane, ethylene, propane, n- and i-butane) and H₂ [16–18], CH₄ reforming with CO₂ or H₂O (gas) to syngas [19–23], partial oxidation of methane to methanol [24–30], and even to benzene [31] are developed in recent years. Among these works, the conversion of CH₄ to syngas and methanol are most studied in photocatalysis. For the desired product of alkanes, such as C₂H₆, the efficiency is still in a low level at present [28,29,32]. As a high-valued product, C₂H₆ is an important industrial raw material to produce C₂H₄, halogenated ethane, and aromatic hydrocarbon

[33–39]. It is therefore necessary to find an effective strategy to improve the yield of C₂H₆.

The H₂ production from water has been a hot topic in photocatalysis, but the use of a sacrificial reagent is necessary [40–44], even in Pt/TiO₂ catalyst system. In addition, the improvement of efficiency via simultaneous utilization of photo-induced electron and hole for two different catalytic reactions is still a rarity. In this work, the two photocatalytic reactions of CH₄ conversion and water splitting into H₂ are introduced simultaneously in one system, and the high-valued products of H₂ and C₂H₆ are gained, which has not been reported. Here the CH₄ is introduced as the sacrificial agent for hole as well as the useful reactant converted into other hydrocarbon. Through this way, the photo-induced electron and hole can be efficiently separated and adequately utilized, and a new strategy about the direct combination of H₂ evolution from water and CH₄ conversion with high efficiency photocatalytic performance is achieved successfully.

2. Experimental methods

2.1. Materials

The commercial P25 (Degussa) is used as TiO₂ precursor. H₂PtCl₆ and CH₃OH were purchased as A.R. grade chemicals from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. 5, 5-dimethyl-1-pyrroline-*N*-oxide (DMPO) was obtained from J&K Chemical Ltd. The CH₄ (with purity ≥ 99.999%) was supplied by

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Fuzhou Xinhang gases co., Ltd. All of the reagents are used without further purification.

2.2. Sample preparation

The commercial TiO_2 was dispersed in H_2PtCl_6 solution with different mass fraction of Pt ($x\% = 0.1\%, 0.3\%, 0.5\%, 1\%, 1.5\%, 2\%$). In the presence of CH_3OH , the mixture was irradiated by UV light of 254 nm for 1 h to produce Pt/ TiO_2 . Then resultant precipitate were harvested by centrifugation, then, washed with deionized water and absolute ethyl alcohol for several times. Finally, the obtained precipitate was dried at 80°C in oven.

2.3. Characterizations

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer with $\text{Cu K}\alpha$ radiation. The diffuse reflectance spectra (DRS) were performed on Varian Cary 500 UV–vis spectrophotometer with BaSO_4 as the background ranging from 250 nm to 800 nm. The morphologies of the obtained products were observed by a transmission electron microscopy (TEM) (FEI Tecnai G2 F20 S-TWIN, operated at an accelerating voltage of 200 kV). X-ray photoelectron spectroscopy (XPS) analysis was collected on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) with monochromatic $\text{Al K}\alpha$ radiation ($E = 1486.2\text{ eV}$). Electron spin resonance (ESR) spectra were obtained using a Bruker model A300 spectrometer with a Philip lamp of 254 nm as light source, and 5,5-dimethyl-L-pyrroline-N-oxide (DMPO) as trapper. All the samples are measured in suspension dispersed in various solutions. The sample is dispersed in purified methanol for detection of $\cdot\text{O}_2^-$, in deionized water for detection of $\cdot\text{OH}$, and in water dissolved CH_4 for detection of $\cdot\text{CH}_3$.

2.4. Evaluation of photocatalytic properties

The photocatalytic activity of the catalyst was measured in a gas-liquid-solid system. 75 mg catalyst was dispersed in 75 mL H_2O , and the CH_4 was filled upon the water with volume of 80 mL (including the gas circuit) at ordinary pressure. The reactant gas was circulated in the system with flow rate of 10 mL/min by a circulating pump. The reactant suspension was irradiated by UV lamps with a wavelength centered at 254 nm (Philips, TUV 4W/G4 T5). The reaction system was remained at 25°C by thermostatic water around. After irradiation for 6 h, the concentration of the gas sample was monitored from the reactor using a gas chromatograph Model HP 6890 (Agilent Technologies Inc., USA) equipped with TDX-01, thermal conductivity detector and flame ionization detector. The schematic of the experimental set up for this work is shown in Fig. S1.

3. Results and discussion

3.1. Morphology and optical properties of the samples

The XRD patterns of the samples with different fraction of Pt ($x\%$) are displayed in Fig. 1. The crystal phase of anatase and rutile TiO_2 in the samples is respectively marked as * and \blacktriangle according to the PDF no. 21–1272 and no. 21–1276 standard card. None of characteristic peaks belonging to Pt are observed due to its low proportion. And with the increasing of Pt proportion, a weak peak at 39.8° is detected, which can be indexed to the (111) plane of Pt (PDF no. 04-0802, labelled by \blacksquare). The intensity of TiO_2 peaks decreases with the amount increasing of Pt. This may be attributed to the shelter of Pt on the surface of TiO_2 particles, or the aggregation inhibition of TiO_2 particles caused by the participation of Pt.

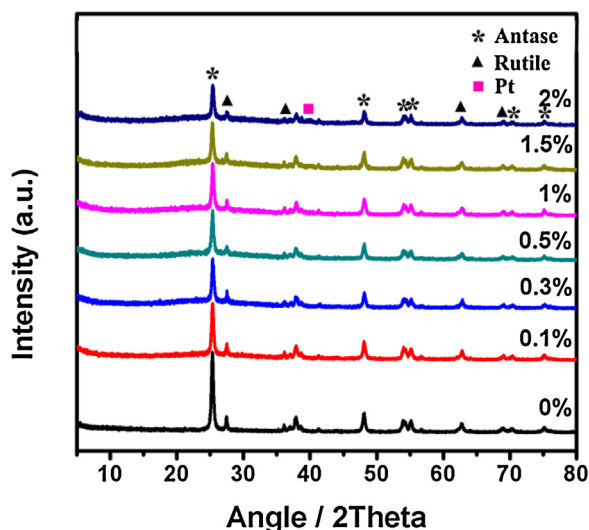


Fig. 1. The XRD patterns of the $x\%$ Pt/ TiO_2 .

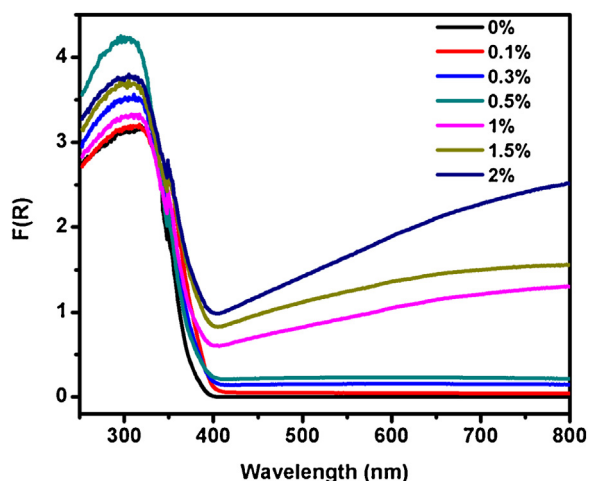


Fig. 2. The UV–vis diffuse reflectance spectra of the $x\%$ Pt/ TiO_2 .

The optical character of the samples was studied by using UV–vis diffuse reflectance spectra (see Fig. 2). It shows that TiO_2 only absorbs the light in the UV region ($\lambda < 400\text{ nm}$), based on which the UV light is used as exciting light source. The introduction of the Pt increases the absorption in the visible light region, and the absorption is positive increased with the proportion of Pt. Besides, the introduction of Pt slightly shifts the absorption edge of the TiO_2 to longer wavelength. The results indicate that the Pt is successfully loaded on the TiO_2 particles.

XPS was carried out to further investigate the surface compositions and chemical states of 0.5% Pt/ TiO_2 and TiO_2 (Fig. 3). From the results spectra of Ti 2p and O 1s of lattice oxygen at 529.8 eV, it shows peak-shifting to the higher binding energy, which can be the evidence for the interaction between Pt and TiO_2 . The peak shifting to the lower binding energy of the oxygen of surface hydroxyl at 531.6 eV [45,46] indicates that Pt is interaction with surface oxygen. The fitted two pairs of Pt peaks are indexed to two states of Pt elements (Pt^0 , Pt^{2+}).

The morphology nature of 0.5% Pt/ TiO_2 is characterized by transmission electron microscopy (TEM) in Fig. 4a. The dispersing Pt particles are smaller as compared to TiO_2 particles. The identification of lattice fringes indicates the coexistence of anatase (A) and rutile (R) TiO_2 , as shown in Fig. 4b. The particle with a deeper contrast of which the diameter is about 5 nm, obtains the lattice fringe

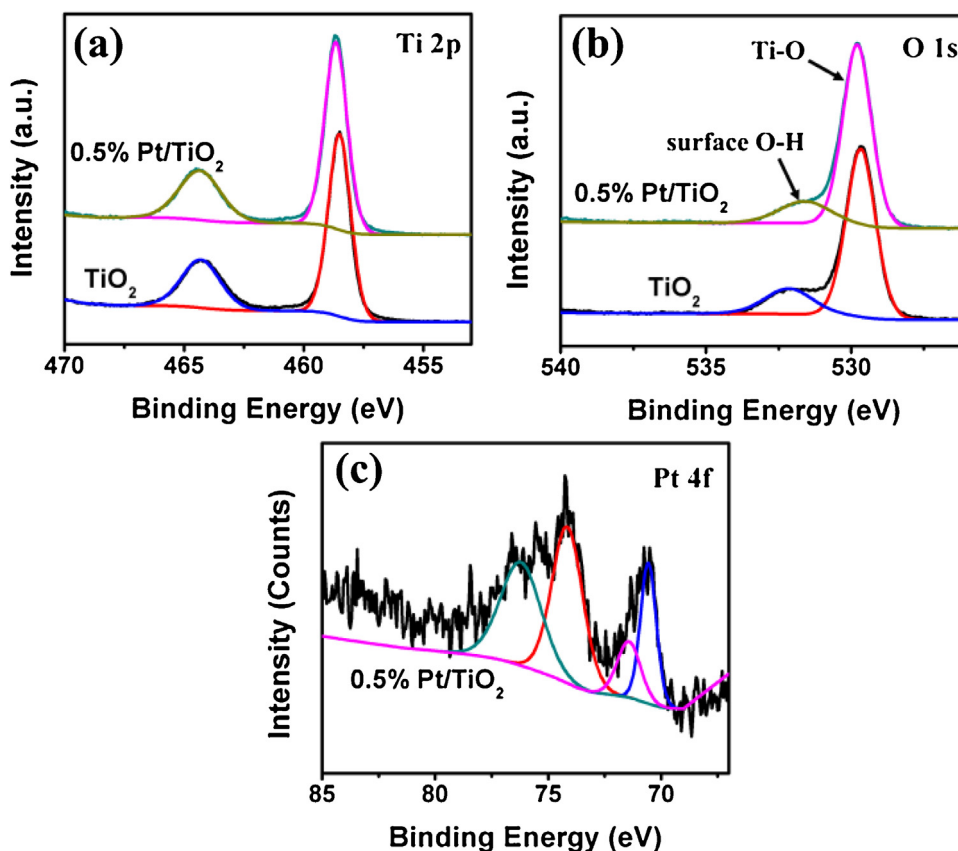


Fig. 3. XPS spectra of 0.5% Pt/TiO₂ and TiO₂: (a) Ti 2p, (b) O 1s, (c) Pt 4f.

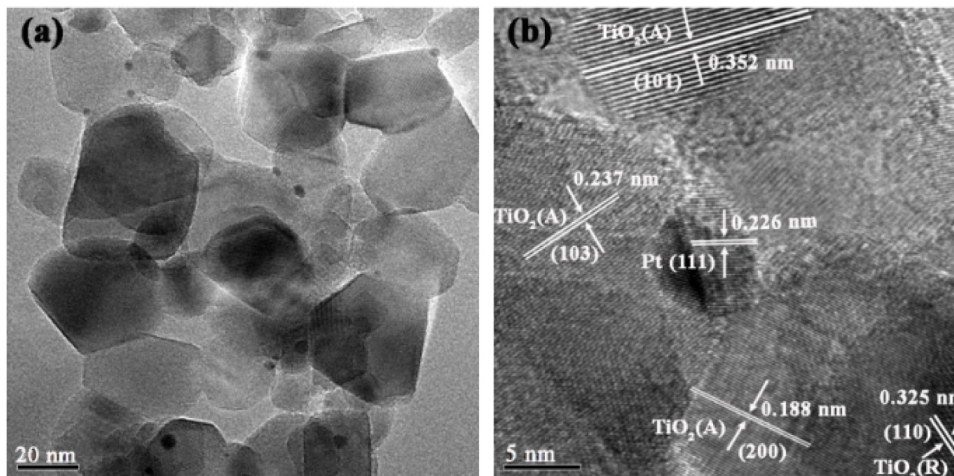


Fig. 4. The TEM (a) and high-resolution TEM (b) images of 0.5% Pt/TiO₂.

indexed to the (111) crystallographic plane of Pt. Therefore, the sample of Pt supported on TiO₂ is successfully prepared.

3.2. Photocatalytic properties of the samples

The photocatalytic activities of x% Pt/TiO₂ are evaluated by the amount of H₂ production (Fig. 5a), the total conversion of CH₄ (Fig. 5b), as well as the distribution of carbonous gas products (Fig. 5c). Unlike the reported literatures on the conversion of CH₄ with liquid H₂O [25,26,28,29,47–49], methanol is hardly detected in this system. It is found that the introduction of Pt obviously improves the amount of all the products. The H₂ production

increases with the increasing of Pt loading, and the maximum of 180 μmol is obtained at Pt fraction of 1.5% (see in Fig. 5a). More Pt (2%) does not result in a continuous increase of the H₂ production. While the total conversion of CH₄ increases with the increasing of Pt loading. The detailed distribution of the carbonous products changes with the increasing of C₂H₆ and decreasing of CO₂ when Pt fraction varies from 0.1% to 0.5%. A little variation of C₂H₆ and increasing of CO₂ can be found with Pt fraction varying from 1% to 2%. All the catalysts obtain little C₂H₄ except 0.5% Pt/TiO₂. And the product of CO over each photocatalyst remains almost constant, which indicates that CO may be the intermediate product for CO₂. Additionally, we can conclude that the participation of Pt changes

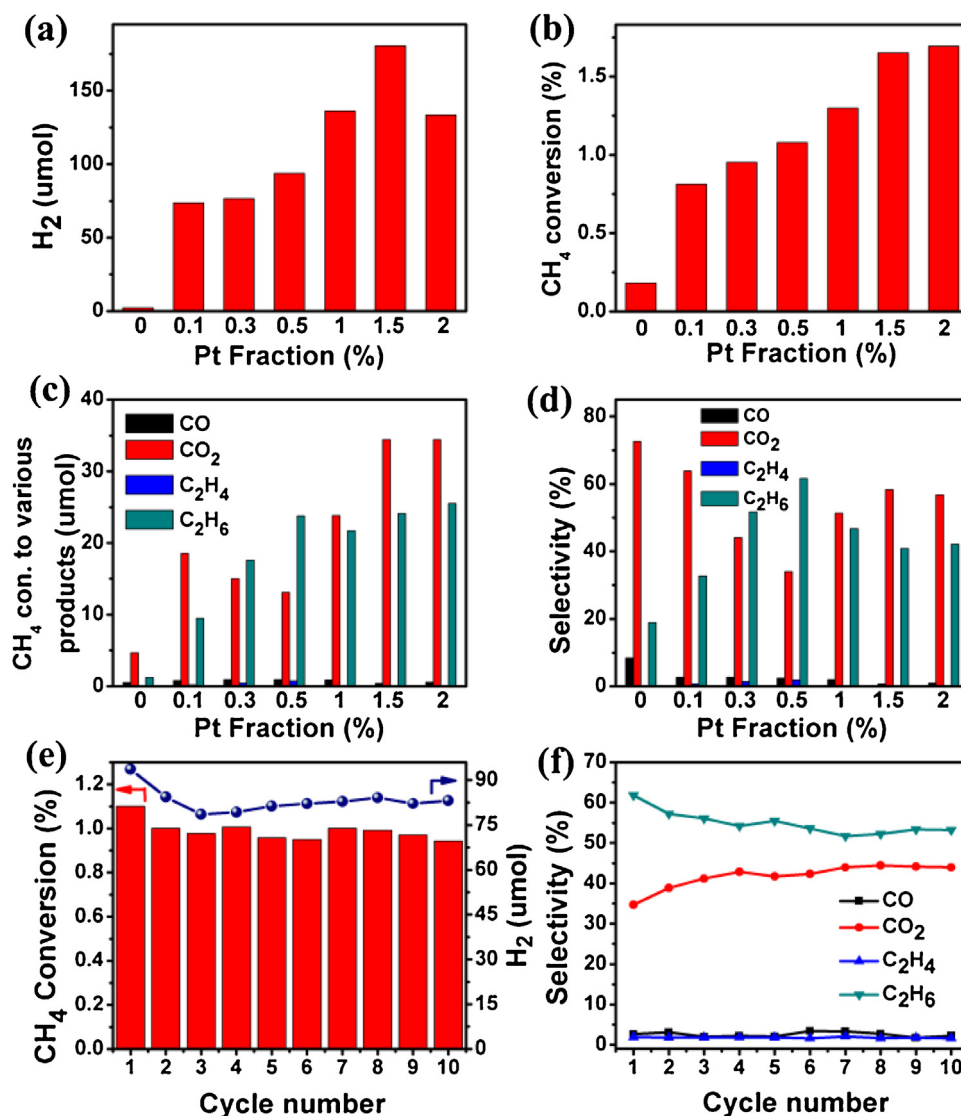


Fig. 5. The photocatalytic activities of (a) H₂ production, (b) CH₄ conversion, (c) CH₄ conversion to various carbonous gas products, (d) selectivity of carbonous products over x% Pt/TiO₂, (e) stability of 0.5% Pt/TiO₂ in the recycling experiment and (f) selectivity of carbonous products over 0.5% Pt/TiO₂ in the recycling experiment. Reaction conditions: 80 mL pure CH₄, 10 mL/min, 75 mg catalyst, 75 mL H₂O, 6 h, ambient condition.

the selectivity of the production of C₂H₆ and CO₂ (Fig. 5d), and 0.5% Pt/TiO₂ exhibits the highest selectivity for C₂H₆ (61.7%). Considering the desired product of C₂H₆, we determine the 0.5% Pt/TiO₂ as the best photocatalyst. Furthermore, it exhibits the considerable stability in the recycling experiment in Fig. 5e. The H₂ production slightly decreases from 93.7 μmol for 1st run to 83.1 μmol for 10th run, and CH₄ conversion decreases from 1.1% for 1st run to 0.94% for 10th run. The selectivity for C₂H₆ still maintains at 53.2% after ten cycles experiment (Fig. 5f).

3.3. Photocatalytic mechanism

The active species are crucial to the photocatalytic reaction, and their roles are examined by means of various scavengers. Ammonium oxalate is used as hole scavenger and Fe³⁺ (Fe(NO₃)₃ added) is used as electron scavenger under the similar reaction condition, and the results are shown in Fig. 6a–c. The trapping of hole dramatically decreases the conversion of CH₄ together with the decreasing of all the carbonous products seen in Fig. 6b and c. While the H₂ production increases from 93.7 μmol to 192.3 μmol in the presence of the trapping of holes (Fig. 6a), and it may be ascribed to the

increased electron availability. Similarly, the trapping of electron dramatically decreases the generation of H₂ (Fig. 6a). On the contrary, it increases the total conversion of CH₄ from 1.08% to 1.5% (Fig. 6b), which may be owed to the increased hole availability. Furthermore, the adding of the electron scavenger decreases the production of C₂H₆ and increases the production of CO₂ simultaneously (Fig. 6c). It seems that the increased hole available tends to mineralize CH₄ into CO₂. It is concluded from the results above that the photo-induced electron contributes to the generation of H₂ while hole is favourable to the conversion of CH₄.

It is well known that Pt/TiO₂ possesses outstanding photocatalytically splitting of water into H₂ with the sacrificial agent for hole [40,50–52]. Is that possible that the participation of CH₄ facilitates the photocatalytic splitting of water into H₂ via consuming more hole? With Ar taking the place of CH₄, the reaction is totally the photocatalytic water splitting. The compared results whether with CH₄ are presented in Fig. 6d (labelled H₂O + CH₄ and H₂O in the figure). It indicates that the introduction of CH₄ improves the H₂ production to almost 3 times. Without participation of H₂O, only a little H₂ is obtained. And it experimentally proves the ability of CH₄ to produce H₂. The results of Table S1 infer that the increasing amount

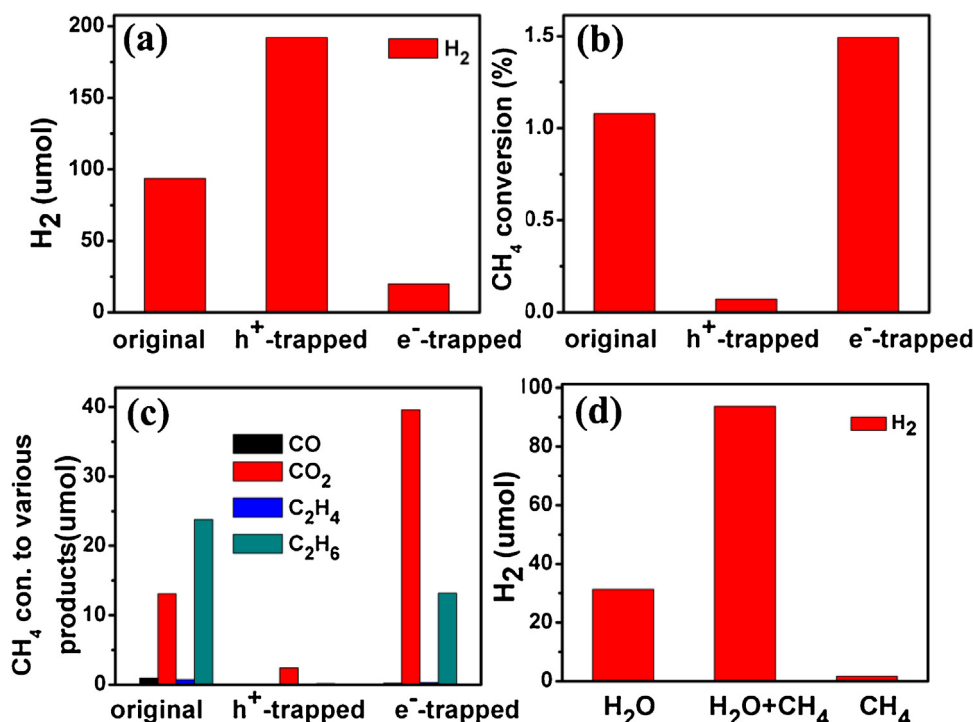


Fig. 6. The photocatalytic activities of (a) H₂ production, (b) CH₄ conversion and (c) carbonous gas product over 0.5% Pt/TiO₂ in various conditions. (d) H₂ production over 0.5% Pt/TiO₂ with various reactants in the system.

of H₂ is mainly derived from the water splitting after the participation of CH₄, while is lesser from CH₄. And it may put down to the improved separation of photo-induced hole and electron, through which way the participation of CH₄ utilizes more holes and finally increases the electron availability. These results well provide the evidences of the synergetic effect for H₂ evolution from water with CH₄ conversion.

It is demonstrated above that the hole and electron play important roles for the yields of carbonous products and H₂. ESR spin-trapping technique with DMPO was conducted to confirm the roles of them or their derivative radicals. It is well known that an electron trapped by an O₂ produces the •O₂⁻, and hereby the signal of •O₂⁻ can be used to investigate the amount of electron. The results of Figure 7a indicate that the introduction of Pt is prone to giving more •O₂⁻, in other words, Pt boosts the separation of photo-induced electrons and holes. Among them, 1.5% Pt/TiO₂ exhibits the strongest signal of •O₂⁻, which is experimentally proved to produce most H₂. It is therefore demonstrated that the electron takes part in the photocatalytic reaction to produce H₂. The •OH is regarded as an oxidizing active species. The signal of •OH gradually decreases along with the increase of the loading of Pt on TiO₂ (Fig. 7b). The •CH₃ presented in Fig. 7c is crucial combining to produce C₂H₆. We can learn that a little of Pt (0.1%) apparently raises the signal vested in •CH₃ [53–56], but more Pt gradually reduces the formation of •CH₃. Moreover, the pure TiO₂ is able to produce the radical of •CH₃, inferring that the CH₄ molecular can be activated and dissociated on the TiO₂ particles. With a little Pt loaded on the surface of TiO₂, the amount of •CH₃ remarkably increases. And it is deduced that the Pt on the surface of TiO₂ particle is favourable to the activation of CH₄. More Pt then reduces the formation of •CH₃, as well as reduces the generation of •OH, it is suggested that •OH may be the key role for •CH₃ formation.

Moreover, the results of XPS indicate that the Pt loading on the surface of TiO₂ particles bonding with the oxygen of surface hydroxyl. And it is confirmed that the surface hydroxyl can be important mediator to generate hydroxyl radical [57,58]. With the

coverage of Pt at the site of surface hydroxyl, it is also verified that the amount of •OH decreases in Fig. 7b, which further confirms the bonding of Pt with oxygen of surface hydroxyl.

It has been widely believed that the transition-metal could activate C–H in CH₄ molecule [59], and it was confirmed that •OH could be effective active species to dehydrogenize CH₄ to form •CH₃ radical [26,27,48,60]. The mechanism should be proposed that with the activation of CH₄ via Pt center, the C–H bond is weakened, and with the dehydrogenization of CH₄ by •OH, the •CH₃ then forms. Based on that Pt loading may reduce the generation of •OH. The increasing of Pt loading may improve the activation of CH₄, but also reduces the amount of •OH since Pt coverage of surface hydroxyl may inhibit the dehydrogenization. Hence the proper Pt loading results in the efficient cooperation between the activation of CH₄ over Pt site and dehydrogenization of CH₄ by •OH, which may be a clue factor for the reaction.

The quantum efficiency (QE) is an important indicator in the determination of photocatalytic reaction. The QE for H₂ production is calculated as 4.7%, which is higher than 2% of which Pt/TiO₂ reacting CH₄ gas with H₂O vapour [61]. The QE for CH₄ conversion is calculated as 3.3% (calculation details seen in the Supporting information).

Thus far, direct combination of the photocatalytic coupling of CH₄ and the synergistic reaction of H₂ evolution from water was studied. It is demonstrated that the introduction of Pt may activate the C–H bond of CH₄ to form more •CH₃, which was consistent with the results of C–H activation at the transition-metal centres [59]. The subsequent coupling of •CH₃ brings up the product of C₂H₆, and the coupling of •CH₂ which is formed by further dehydrogenation from •CH₃ leads to the generation of C₂H₄. Based on the fact that a little C₂H₄ and no C₂H₂ formed in the reaction system, it is considered difficult to further generate •CH₂ from •CH₃ and hardly possible to yield •CH from •CH₂. Thereby the generation of CO₂ is attributed to the oxidation of CH₄ or •CH₃ by hole or molecule oxygen (generated from water splitting). Focusing on the performance of photo-generated electron, it will react with H⁺ to

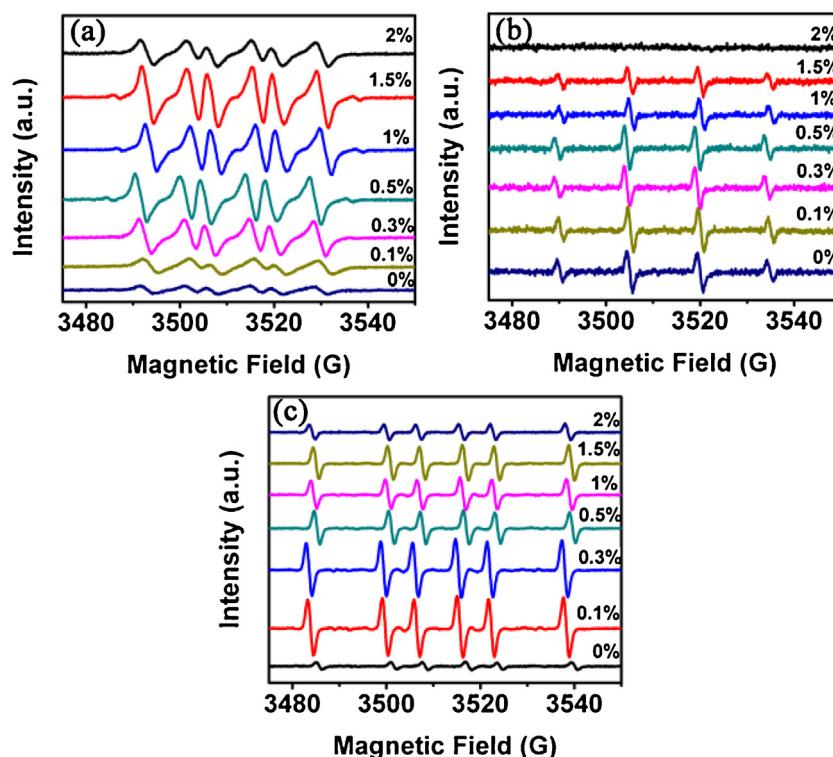
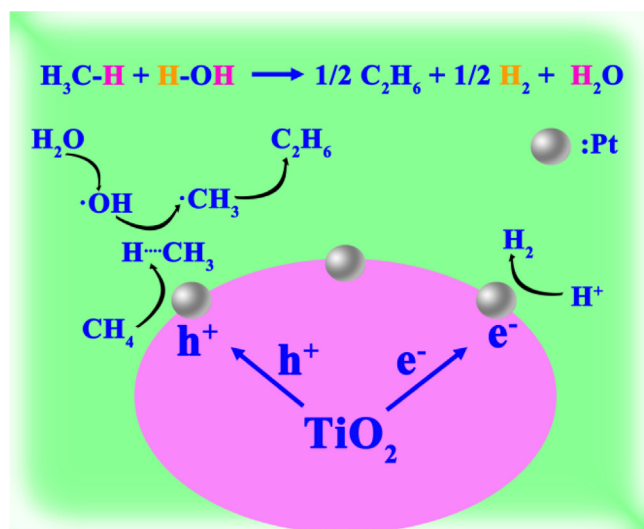
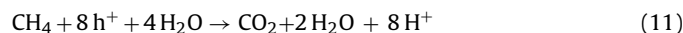
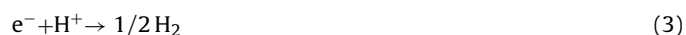


Fig. 7. ESR spectra of $\text{O}_2^{\bullet-}$ (a), $\bullet\text{OH}$ (b) and $\bullet\text{CH}_3$ (c) radical species trapped by DMPO over Pt/TiO₂ series dispersions.



Scheme 1. The proposed mechanism of the photocatalytic process.

gives rise to the generation of H_2 . The photocatalytic mechanism is proposed in Scheme 1, and the processes are hypothesized as follow:



4. Conclusions

In summary, we describe a new synergistic photocatalytic system in which the coupling of CH_4 to high-valued products plays an important role in enhancing the photocatalytic splitting of water into H_2 . The Pt loading on TiO_2 is an efficient way to improve the yields of both H_2 and C_2H_6 products. The synergistic effect between the two involved reactions gives more efficient separation and adequate utilization of photo-induced electron and hole, and the photo-induced electron contributes to the generation of H_2 while hole is favourable to the conversion of CH_4 . The proper Pt loading results in the efficient cooperation between the activation of CH_4 over Pt site and dehydrogenation of CH_4 by $\bullet\text{OH}$, afterward appropriate amount of $\bullet\text{CH}_3$ is produced, and then C_2H_6 is formed. The new strategy of the photocatalytic reaction realizes synergistically selective coupling of CH_4 and H_2 production from aqueous water, and improves the efficiency in photocatalysis (with QE of 4.7% for H_2 generation and 3.3% for CH_4 conversion). We believe that the bridged photocatalytic pathway can provide some valuable information for extending water-gas reactions in future.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.11.039>.

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